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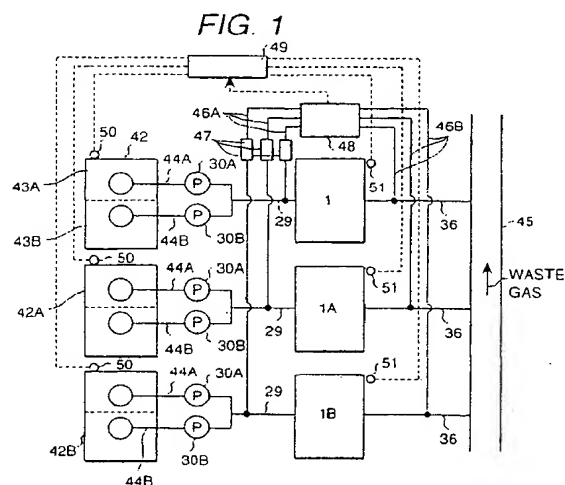
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(54) A method for processing perfluorocarbon and an apparatus therefor

(57) An exhaust gas containing a perfluoride compound (PFC) and  $\text{SiF}_4$  is conducted into a silicon remover and contacted with water. A reaction water supplied from a water supplying piping and air supplied from an air supplying piping are mixed with the exhaust gas exhausted from the silicon remover. The exhaust gas containing water, air, and  $\text{CF}_4$  is heated at 700 °C by a heater. The exhaust gas containing PFC is conducted to a catalyst layer filled with an alumina group catalyst. The PFC is decomposed to HF and  $\text{CO}_2$  by the catalyst. The exhaust gas containing HF and  $\text{CO}_2$  at a high temperature exhausted from the catalyst layer is cooled in a cooling apparatus. Subsequently, the exhaust gas is conducted to an acidic gas removing apparatus to remove HF. In accordance with the present invention, the silicon component is removed from the exhaust gas before introducing the exhaust gas into the catalyst layer. Therefore, surface of the catalyst can be utilized effectively, and the decomposition reaction of the perfluoride compound can be improved.



## Description

[0001] The present invention relates to a method for processing perfluorocarbon and an apparatus therefor, and particularly, a preferable method for applying to process perfluorocarbon (hereinafter, called PFC) contained in an exhaust gas from a semiconductor manufacturing plant, and an apparatus therefor.

[0002] In accordance with a semiconductor manufacturing process, PFC gases, which are harmless to human being, non explosive, and easy for handling, such as  $\text{CF}_4$  and the like are used as an etchant in a dry etching process, and such as  $\text{C}_2\text{F}_6$  and the like are used as a cleaning gas in a CVD process. These PFC gases are ionized by plasma discharge of a high voltage after introducing into an etching apparatus or a CVD apparatus, and perform etching or cleaning of wafers in an active radical state.

[0003] However, the amount of PFC gas actually consumed in the etching or the cleaning is a several % to tens % by volume.

[0004] Rest of the PFC gas are exhausted outside the system in an unreacted state.

Table 1

No	PFC gas	Properties of gas			Consume in Japan (t/year)	Main use
		Warm. coeff. <sup>1)</sup>	Life <sup>2)</sup> (year)	Toxic. react. <sup>3)</sup>		
1	$\text{CF}_4$ <sup>4)</sup>	6,300	50,000	low-toxic. non-flam. <sup>5)</sup>	300('94) 394('95)	Etching gas: 75% CVD cleaning gas: 25%
2	$\text{CF}_6$ <sup>6)</sup>	12,500	10,000	low-toxic, non-flam. <sup>5)</sup>	4('94) 200('95)	P-CVD cleaning gas
3	$\text{NF}_3$ <sup>7)</sup>	9,720	179	toxic	25('94) 39('95)	CVD cleaning gas: 92% IC-Etching gas: 8%
4	$\text{CHF}_3$ <sup>8)</sup>	12,100	250	-	55('94)	dry etching
5	$\text{C}_4\text{F}_8$ <sup>9)</sup>	8,700	3,200	-	-	etching
6	$\text{C}_3\text{F}_8$ <sup>10)</sup>	7,000	2,600	-	-	P-CVD cleaning gas
7	$\text{SF}_6$ <sup>11)</sup>	24,900	3,200	-	26('94)	dry etching: 90% CVD cleaning gas: 10%

## Remarks:

1) Warming-up coefficient

2) Life time in atmosphere

3) Toxicity and reactivity

4) Flon 14

5) Non-flammable

6) Flon 116

7) Nitrogen trifluoride

8) Flon 23

9) Flon C 318

10) Flon 218

11) Sulfur hexafluoride

[0005] Because a fluorine atom has a small atomic radius and a strong bonding force, PFC, a compound of fluorine atoms, has stable characteristics. PFC includes flon such as FC (fluorocarbon) and HFC (hydrofluorocarbon), which do not include chlorine, and perfluoride compounds such as nitrogen trifluoride ( $\text{NF}_3$ ), and sulfur hexafluoride ( $\text{SF}_6$ ). Main materials of PFC, and their characteristics and main use are indicated in Table 1.

[0006] PFC exists stably in atmosphere for a long time, because it does not contain chlorine, its molecular structure is compact, and its bonding force is strong. For instance, a life of  $\text{CF}_4$  is as long as 50,000 years,  $\text{C}_2\text{F}_6$  is 10,000 years, and  $\text{SF}_6$  is 3,200 years. However, PFC has a large warming-up coefficient. In comparison with  $\text{CO}_2$ ,  $\text{CF}_4$  is 6,500 times,

$C_2F_6$  is 9,200 times, and  $SF_6$  is 23,900 times. Therefore, although PFC has a smaller releasing amount than  $CO_2$  which is required to be decreased as a cause of warming-up the earth, release of the PFC is anticipated to be certainly restricted in near future. In this case, a countermeasure against the exhaust gas from semiconductor manufacturing plants, which occupies a majority of the PFC releasing amount, will become important.

**[0007]** For instance, in accordance with an etching step in the semiconductor manufacturing plant, a PFC gas for etching is supplied into a chamber. A part of the PFC gas is converted to highly corrosive fluorine atoms by applying plasma. The fluorine atoms perform an etching of silicon wafers. The exhaust gas from the chamber is pumped out continuously by a vacuum pump. In order to prevent corrosion by the acidic gas, purging of the exhaust gas with nitrogen gas is performed. The exhaust gas contains nitrogen of 99%, and the PFC of residual 1%, which has not been used for the etching. The exhaust gas pumped out by the vacuum pump is conducted to an acid removing apparatus through the duct for removing the acidic gas, and released to atmosphere as a state containing the PFC.

**[0008]** In the semiconductor manufacturing plants, a reagent method and a combustion method have been used practically as a decomposition method of the PFC. The former is a method, wherein fluorine is chemically fixed at approximately 400 ~ 900 °C by using a special reagent. In accordance with this method, an exhaust gas processing is not necessary, because any of acidic gas is not generated by decomposition. The latter is a method, wherein the PFC gas is conducted to a combustor, and decomposed thermally in a flame at least 1,000 °C generated by combustion of LPG and propane gas.

**[0009]** In accordance with the above reagent method, the reagent reacted chemically with the PFC can not be re-used, and the expensive reagent, which is consumed in the reaction as a consumable article, is required to be supplied frequently. Therefore, the operation cost is 10 to 20 times in comparison with the combustion method. Furthermore, because an amount of the reagent equivalent to the amount of the PFC to be processed is necessary, a practical equipment for the reagent method requires a large installing area such as approximately 3 ~ 5 m<sup>2</sup>.

**[0010]** In accordance with the above combustion method, the thermal decomposition is performed at a high temperature such as at least 1,000 °C for  $C_2F_6$  and at least 1,100 °C for  $CF_4$ , and a large amount of thermal energy is required. Furthermore, the combustion method generates NOx and a large amount of  $CO_2$  by combustion at a high temperature. Because the PFC is exhausted in a state diluted with inactive  $N_2$  gas, a potential of miss-fire is high, and a sufficient operation control is required.

**[0011]** An application of the combustion method to the semiconductor manufacturing process has been studied. The PFC is exhausted as a mixed gas diluted with  $N_2$  gas to be a concentration of a several %. Accordingly, in combustion of the mixed gas, a large amount of air for combustion is required in addition to a fuel gas. Consequently, because the amount of gas to be processed is increased, size of the apparatus is increased, and the installing area for the apparatus is required to be as large as approximately 0.7 ~ 5 m<sup>2</sup>.

**[0012]** For instance, when  $C_2F_6$  is contained by 1 % in an exhaust gas exhausted by 100 liter/min. from a semiconductor manufacturing process, a necessary amount of LPG to make the thermal decomposition temperature at least 1,000 °C is 10 liter/min. and a necessary amount of air is approximately 400 liter/min. with an excessive ratio of 1.5. The total amount of the exhaust gas after the combustion becomes approximately 500 liter/min., because oxygen in the air is consumed and  $CO_2$  is generated by 30 liter/min. The total amount of the exhaust gas is increased almost 5 times of the exhaust gas exhausted from the semiconductor manufacturing process. The semiconductor manufacturing plant has a large restriction in space, because the plant must be clean rooms. Accordingly, it is difficult to keep the necessary area for installing a new exhaust gas processing apparatus in a previously built semiconductor manufacturing plant.

**[0013]** On the other hand, a catalytic method, wherein the PFC is decomposed at approximately 400 °C, is applied to CFC (chlorofluorocarbon) and HCFC (hydrochlorofluorocarbon), which have similar chemical compositions with the PFC and an ozone destruction effect. Because the CFC and HFC contain chlorine atoms having a large atomic radius in their compositions, the molecular structures composed by bonding fluorine atoms and hydrogen atoms having a small atomic radius are distorted. Therefore, the CFC and HFC can be decomposed at a relatively low temperature.

**[0014]** A method for decomposing CFC (or HFC) using a catalyst was disclosed in JP-A-9-880 (1997). In accordance with the above method, a mixed gas of heated air, which is a carrier gas, steam, and CFC is conducted to a catalyst layer. The temperature of the catalyst layer is approximately 430 °C, because CFC has a low decomposition temperature. The exhaust gas containing decomposed gases exhausted out from the catalyst layer is cooled rapidly with cooling water, because of preventing generation of dioxine.

**[0015]** Preferably the present invention provides a method for processing perfluorocarbon using a catalyst, which can improve the decomposition reaction, and an apparatus therefor.

**[0016]** The first aspect of the invention is in the steps of removing silicon components from an exhaust gas containing a perfluoride compound and the silicon components, subsequently, supplying the exhaust gas containing the perfluoride compound, to which any of water or steam is added, to a catalyst layer which is filled with a catalyst, to decompose the perfluoride compound with the catalyst.

**[0017]** In accordance with the first aspect, closing pores formed on the catalyst by solid particles generated by a

reaction of the silicon components in the exhaust gas with the water or the steam added to the exhaust gas can be prevented, because the silicon components in the exhaust gas to be supplied to the catalyst is removed previously. Furthermore, in accordance with the first aspect, choking intervals formed among the catalysts by the solid particles can be prevented. Accordingly, since the surface of the catalysts can be utilized effectively, the decomposition reaction of the perfluoride compound can be improved by the first invention. The decomposition efficiency of the perfluoride compound can be improved by the first invention.

[0018] The second aspect of the invention is in the step of removing acidic gas from a cooled exhaust gas. In accordance with the step, the acidic gas contained in the exhaust gas is decreased significantly.

[0019] The third aspect of the invention is in the steps of removing the silicon components from the exhaust gas by a first silicon components removing apparatus and a second silicon components removing apparatus. The exhaust gas flowed out from the first silicon components removing apparatus is supplied to the second silicon components removing apparatus to make the exhaust gas contact with water in the second silicon components removing apparatus. In the first silicon components removing apparatus, the exhaust gas containing the silicon components are contacted with waste water from the second silicon components removing apparatus and cooling water contacted with the exhaust gas containing a decomposed gas.

[0020] Because the waste water from the second silicon components removing apparatus and cooling water contacted with the exhaust gas containing the decomposed gas are contacted with the exhaust gas containing the silicon components in the first silicon components removing apparatus, a part of the silicon components contained in the exhaust gas is removed with a mixed water of the waste water and the cooling water. Therefore, in amount of fresh water to be supplied to the second silicon components removing apparatus can be decreased, and an amount of waste water to be processed is decreased. Furthermore, since the silicon components contained in the exhaust gas are processed twice to be removed by the first and second silicon components removing apparatus, respectively, the removing efficiency of the silicon components are improved.

[0021] The fourth aspect of the invention is in using an alumina group catalyst as the catalyst for decomposing the perfluoride compound.

[0022] Because using the alumina group catalyst, the perfluoride compound can be decomposed effectively and conveniently at a reaction temperature in the range of 650 ~ 750 °C.

#### BRIEF DESCRIPTION OF THE DRAWINGS

##### [0023]

FIG. 1 is a flow sheet of an exhaust gas control system for a dry etching apparatus in a semiconductor manufacturing plant, a preferable embodiment of the present invention, i.e. a perfluoride processing apparatus, is applied thereto, FIG. 2 is a schematic illustration indicating a composition of a clean room, wherein the dry etching apparatus and the perfluoride compound processing apparatus indicated in FIG. 1 are arranged,

FIG. 3 is a flow sheet indicating a composition of the perfluoride compound processing apparatus indicated in FIG. 1 and FIG. 2,

Fig. 4 is a schematic vertical cross section of the silicon remover indicated in FIG. 3,

FIG. 5 is a detailed vertical cross section of the PFC decomposition processing unit indicated in FIG. 3,

FIG. 6 is a graph for explanation indicating decomposition characteristics of various PFC by the alumina group catalyst,

FIG. 7 is a schematic partial vertical cross section for explanation indicating an exchanging operation of a catalyst cartridge indicated in FIG. 5,

FIG. 8 is a flow sheet of another embodiment of the perfluoride processing apparatus indicated in FIG. 1,

FIG. 9 is a schematic vertical cross section of another embodiment of the PFC decomposition processing unit,

FIG. 10 a schematic illustration of another embodiment of the clean room, wherein another embodiment of the perfluoride compound processing apparatus and dry etching apparatus are arranged,

FIG. 11 is a flow sheet indicating a composition of the perfluoride compound processing apparatus indicated in FIG. 10,

FIG. 12 is a schematic cross section in the vicinity of the baffle plate indicated in FIG. 11,

FIG. 13 is a schematic vertical cross section of another embodiment of the perfluoride compound processing apparatus indicated in FIG. 1, and

FIG. 14 is a flow sheet indicating a composition of another embodiment of the perfluoride compound processing apparatus indicated in FIG. 1.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0024]** A perfluoride compound processing apparatus (PFC gas processing apparatus), i.e. a preferred embodiment of the present invention applied to an exhaust gas control system of an etching apparatus in a semiconductor manufacturing plant, is explained hereinafter referring to FIG. 1, FIG. 2, and FIG. 3.

**[0025]** The PFC does not contain chlorine, its molecular structure is compact, its bonding force is strong, and its decomposition temperature is as high as approximately 700 °C. Therefore, the catalytic method (disclosed in JP-A-9-880 (1997)), which could be applied to the CFC and HFC, could not be applied to the PFC. However, currently, the inventors of the present application have succeeded in development of an alumina group catalyst having a reaction temperature at approximately 700 °C applicable to the decomposition of PFC. Regarding the above catalyst, patent applications are filed to the Japanese Patent Office as Japanese Patent Applications No. Hei 9-4349 (filed January 14, 1997) and No. Hei 9-163717 (filed June 20, 1997). In accordance with the present embodiments, the above catalyst are used for processing the exhaust gas.

**[0026]** In accordance with the exhaust gas control system of the dry etching apparatus, for instance, each of PFC processing apparatus 1, 1A, 1B, is connected to each of three dry etching apparatus 42 as indicated in FIG. 1. Each of the dry etching apparatus 42 comprises two etching regions 43A, 43B, partitioned in the apparatus.

**[0027]** In each of the etching regions, an etching process is performed for wafers by supplying CF<sub>4</sub>, i.e. a PFC gas, as an etching gas. The exhaust gas from the etching regions 43A, 43B, is conducted to a PFC processing apparatus 1 through piping 44A, 44B, 29, by driving vacuum pumps 30A, 30B. The exhaust gas contains approximately 1 % of CF<sub>4</sub>, which has not been consumed in the etching process, and SiF<sub>4</sub> generated by the etching process. The exhaust gas is exhausted to the duct 45 after processed in the PFC processing apparatus 1 through the piping 36. The exhausted gases from other dry etching apparatus 42 are also conducted to the duct 45.

**[0028]** Each of the exhaust gas in the piping 29 and the exhaust gas in the piping 36 is conducted to a gas chromatography by sampling piping of 46A and 46B, respectively. An acid gas filter 47 is provided in the sampling piping 46A. Concentrations of CF<sub>4</sub> in the exhausted gases supplied to and exhausted from the PFC processing apparatus 1 are determined by the chromatography 40. The determined values on the concentration of CF<sub>4</sub> in the exhausted gases are input to a monitoring apparatus 49. When the concentration of CF<sub>4</sub> in the exhausted gas in the piping 36 is higher than a first preset value, the monitoring apparatus 49 generates an alarm sound with flashing a warning device 51 of the corresponding PFC processing apparatus for warning generation of an abnormal state. When the concentration of CF<sub>4</sub> in the exhausted gas in the piping 29 is higher than a second preset value, the monitoring apparatus 49 generates an alarm sound with flashing a warning device 50 of the corresponding dry etching apparatus 42 for warning generation of an abnormal state. Furthermore, the monitoring apparatus 49 checks a normality of the catalytic reaction in the reactor 9, which will be explained later, and a catalyst change timing from deterioration of the catalyst, based on a decomposition ratio obtained from the concentrations of CF<sub>4</sub> at the entrance and the outlet of the PFC processing apparatus 1.

**[0029]** Next, an approximate arrangement of the above exhaust gas control system in the clean rooms of the semiconductor manufacturing plant is explained hereinafter referring to FIG. 2. A building 59 of the semiconductor manufacturing plant is composed of clean rooms 53, 54, at both an upper side and a lower side of grating 52, respectively. Air in the clean room 54 is cleaned by filters 55A, 55B, and conducted to the clean room 53 through the piping 57A, 57B, by driving blowers 55A, 55B. The air is cleaned again by the filter 58. The clean room 53 has a higher cleanliness than the clean room 54. The dry etching apparatus 42 is installed in the clean room 53, i.e. a manufacturing apparatus area. The PFC processing apparatus 1, 1A, and the like, and the vacuum pumps 30A, 30B, are installed in the auxiliary apparatus area in the clean room 54. The piping such as piping 44A, duct 45, and the like are arranged at the piping area above the auxiliary apparatus area in the clean room 54.

**[0030]** A composition of the PFC processing apparatus is explained hereinafter referring to FIG. 3. The compositions of the PFC processing apparatus 1A, 1B, are as same as the composition of the PFC processing apparatus 1. The PFC processing apparatus comprises a silicon remover 2, a heating apparatus 3, a reactor containing a catalyst layer 11, a cooling apparatus 22, an acidic gas removing apparatus 98, a blower 59, a waste water pump 60, and a temperature controller 62. The exhaust gas exhausted from the blower 30A is conducted to the duct 45 through the silicon remover 2, the heating apparatus 3, the reactor, the cooling apparatus 22, the acidic gas removing apparatus 98, and the blower 59. The heating apparatus 3, the reactor 9, and the cooling apparatus 22 are assembled in an integral body as indicated in FIG. 5, and composed of a PFC decomposition processing unit 76.

**[0031]** A detailed composition of the silicon remover 2 is indicated in FIG. 4. The silicon remover 2 comprises a spray 26 and a diffusion portion 27 filled with packing materials inside its vessel. The exhaust gas containing CF<sub>4</sub>, SiF<sub>4</sub>, and the like as impurities is conducted into the vessel of the silicon remover 2 via the piping 29. The exhaust gas outlet of the piping 29 in the vessel is oriented downwards. The exhaust gas flows upwards in the vessel, and passes through the diffusion portion 27 to diffuse and to flow in the vessel. Cooling water supplied from a water supplying pipe 38 is sprayed through the spray 26. The diffusion portion 27 increases a contacting ratio of the sprayed water and the exhaust

gas, and improves removing performance for the impurities as explained later.

**[0032]** A reaction expressed by the following equation (1) is generated by contacting  $\text{SiF}_4$  contained in the exhaust gas with the sprayed water, and the  $\text{SiF}_4$  contained in the exhaust gas is decomposed to  $\text{SiO}_2$  and HF.



**[0033]** The generated  $\text{SiO}_2$  is fine particles of solid body, and removed from the exhaust gas by the sprayed water concurrently with its generation. HF has a large solubility in water, and is removed from the exhaust gas by dissolution into water. The waste water containing  $\text{SiO}_2$  and HF is conducted to the bottom portion of the acid gas removing apparatus 26 through the piping 35. The impurities accompanied with the exhaust gas can be removed, not by spraying water, but by contacting with water by a bubbling method.

**[0034]** Because the outlet of the exhaust gas piping 29 is oriented downwards, sprayed water from the spray 26 is prevented from splashing and back flowing into the piping 26. The vessel of the silicon remover 2 is made of vinyl chloride, which is corrosion resistant against HF, in order to protect the vessel from the corrosion by HF, which is generated by the reaction expressed by the equation (1).

**[0035]** A ball check valve 27 is provided at the exhaust gas outlet portion of the silicon remover 2. The ball check valve 27 is arranged between the ring shaped protrusion 28A and the protrusion 28B. Therefore, the silicon remover 2 made of vinyl chloride is protected from receiving a thermal damage by a back flow of a hot gas from its downstream, i.e. the heating apparatus 3, when an operation of the PFC processing apparatus 1 is stopped.

**[0036]** The exhaust gas flowing out from the silicon remover 2 is conducted to the PFC decomposition processing unit 76 through the piping 31.

**[0037]** Detailed composition of the PFC decomposition processing unit 76 is indicated in FIG. 5. The PFC decomposition processing unit 76 comprises a heating apparatus 3, a reactor 9, and a cooling apparatus 22. A casing 6 and an internal tube 7 is shared with the heating apparatus 3 and the reactor 9. A diameter of the internal tube 7 is smaller at the upper portion than the lower portion of the pipe 7. A lid 87 to be connected to the piping 31 is provided on the upper end of the casing 6. A flange 12 of the internal pipe 7 is fixed to the flange 13 of the casing 6 by bolts. The heating apparatus 3 and the reactor 9 are composed to form an integral body structure. The upper end portion of the internal tube 7 is restricted in moving in a horizontal direction by a cylindrical portion 14 provided on the lid 87. A ring shaped plate 8 is provided on the internal tube 7.

**[0038]** The heating apparatus 3 comprises a electric heater 4 and a thermal insulating material 5 covering the heater is arranged above the ring shaped plate 8. The heater 4 and the insulating material 5 are arranged between the casing 6 and the internal tube 7. A gap 16 is formed between the casing 6 and the ring shaped plate 8. The gap 16 prevents the casing 6 from being conducted with heat of the high temperature exhausted gas (700 °C) from the internal tube 7 and the ring shaped plate 8, and releasing the heat outside the casing 6. That means, A heat loss of the exhaust gas can be reduced. The structure of the PFC processing apparatus 1 can be simplified by forming an integral body structure with the heating apparatus 3 and the reactor 9.

**[0039]** The reactor 9 is arranged at a position lower than the ring shaped plate 8. The reactor 9 comprises a catalyst cartridge 10 containing a catalyst layer 11 formed by filling an alumina group catalyst on a metallic mesh 16. The alumina group catalyst is a catalyst containing  $\text{Al}_2\text{O}_3$  of 80 % and  $\text{NiO}_2$  of 20 %. The catalyst cartridge 10 is inserted into the internal tube 7. A cylinder 17 is fixed to the casing 6 by joining the flange 18 with the flange 13. The flange 63 of the catalyst cartridge 10 is combined and held by the flange 13. The reactor 9 comprises a heater for keeping the reactor at a temperature (not shown in the figure) arranged between the casing 6 and the internal tube 7. A baffle holder 21 holding a baffle 20 is fixed to the cylinder 17. The cooling apparatus 22 is arranged at beneath the baffle holder 21, and fixed to the baffle holder 21. Sprays 25 and 26 are provided inside the casing of the cooling apparatus 22.

**[0040]** Reaction water, or steam, supplied from the water supplying pipe 32, and air supplied from the air supplying pipe 41 are mixed with the exhaust gas in the piping 31. The water is supplied into the exhaust gas, because the chemical reaction expressed by the equation (2) explained later is a hydrolysis reaction. The supplying amount of water, or steam, is approximately 25 times per one mole of  $\text{CF}_4$ . The exhaust gas containing water, air, and  $\text{CF}_4$  is heated indirectly by the electric heater 4 during flowing through a path 15 in the heating apparatus 3. Then, the water is converted to steam. The exhaust gas is heated by the electric heater 4 to approximately 700 °C, i.e. a temperature that the decomposition of  $\text{CF}_4$  is preferably proceeded in the catalyst layer. The temperature control apparatus 30 controls the current flowing the electric heater 4 so that the temperature  $T_e$  of the exhaust gas determined by the thermometer 61 at the inlet portion 94 of the reactor 9 becomes a preset temperature. This temperature control is used in the following respective of embodiments. The temperature of the catalyst layer 11 can be maintained at the reaction temperature by the above temperature control. In a case of  $\text{CF}_4$ , the temperature is maintained in the range of approximately 650 ~ 750 °C.

[0041] The heated exhaust gas containing  $\text{CF}_4$  is supplied to the reactor 9 filled with the catalyst. The  $\text{CF}_4$  in the exhaust gas is reacted with  $\text{H}_2\text{O}$  and decomposed to  $\text{HF}$  and  $\text{CO}_2$  by the effect of the alumina group catalyst in the catalyst layer 11 as expressed by the following equation (2):



[0042] In a case when  $\text{C}_2\text{F}_6$ , one of the PFC, is contained in the exhaust gas,  $\text{C}_2\text{F}_6$  is decomposed to  $\text{CO}_2$  and  $\text{HF}$  by the reaction expressed by the following equation (3):



FIG. 6 is a graph indicating decomposition characteristics of the PFC by the alumina group catalyst, and the abscissa indicates decomposition temperature and the ordinate indicates decomposition rate. The alumina group catalyst used in the measurement had the composition explained previously. Tested gases were four kinds of PFC, such as  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_4\text{F}_8$ . As the testing conditions, the concentration of respective PFC was 0.5 %, and SV was 1000/h. The reaction water was added approximately 10 times of a theoretical amount. As FIG. 6 reveals, all the four PFC indicated the decomposition rate near 100 % at a reaction temperature of approximately 700 °C. The decomposition rate of  $\text{CF}_4$  and  $\text{CHF}_3$  at approximately 650 °C is equal to or more than 95 %, and the decomposition rate of  $\text{C}_2\text{F}_6$  and  $\text{C}_4\text{F}_8$  at approximately 670 °C is equal to or more than 80 %. By using the above catalysts, practical decomposition of the PFC in the range of approximately 650 ~ 750 °C become possible.

[0043] The high temperature exhaust gas containing the decomposed gases such as  $\text{CO}_2$  and  $\text{HF}$  exhausted from the catalyst layer 11 is conducted to the cooling region 23 in the cooling apparatus 22 through the baffle 20.

[0044] The cooling water supplied throughout the water supplying piping 39, and 40 are sprayed continuously in to the cooling region 23 by the sprays 24 and 25. The exhaust gas at a high temperature is cooled to 100 °C or lower by the sprayed water. A part of  $\text{HF}$  is removed from the exhaust gas by dissolving into the cooling water. The cooling of the exhaust gas at a high temperature can be achieved not by spraying but by bubbling the gas into a water tank. The sprayed water is conducted to a lower portion of the acidic gas removing apparatus 98 through the piping 34 and 35. In accordance with the provided baffle 20, the path for conducting the exhaust gas from the baffle holder 21 to the cooling apparatus 22 becomes zigzag, and a back flow of the splashed cooling water sprayed from the sprays 24 and 25 into the catalyst layer 11 can be prevented. Therefore, a temperature drop of the catalyst layer 11 by the splashed water can be prevented, and release of undecomposed PFC can be avoided.

[0045] The exhaust gas containing the decomposed gases ( $\text{CO}_2$  and  $\text{HF}$ ) at a low temperature exhausted from the cooling apparatus 22 is conducted to the acidic gas removing apparatus 98 through the piping 33. The acidic gas removing apparatus 98 comprises a packed layer 95 filled with Raschig rings made of plastics and a spray 27 inside for removing  $\text{HF}$  contained in the decomposed gas by a high concentration such as approximately 4 % by volume. The spray 27 is arranged at above the packed layer 95. The cooling water supplied through the water supply piping 70 is sprayed through the spray 27. The cooling water is flowed down through the packed layer 95. The exhaust gas is contacted sufficiently with the cooling water in the packed layer 95, and a majority of the  $\text{HF}$  contained in the exhaust gas can be dissolved into the cooling water. The  $\text{HF}$  in the exhaust gas can be removed significantly by the acidic gas removing apparatus 98 from 4 % by volume to a several ppm.

[0046] The exhaust gas, of which acidic gas content is decreased remarkably, is conducted to the duct 45 through the piping 36 by operating a blower 59, and released outside the system. Inside the cooling apparatus 22 and the acidic gas removing apparatus 98 are kept at a negative pressure by the operation of the blower 59. Leaking the hazardous  $\text{HF}$  contained in the exhaust gas to outside the system can be prevented. The bubbling method also can be applied to the acidic gas removing apparatus 98. However, in accordance with the spraying method, a pressure loss is smaller than the bubbling method, and the capacity of the blower 59 can be made small.

[0047] The waste water generated at the silicon removing apparatus 2, the cooling apparatus 22, and the acidic gas removing apparatus 98 are gathered together once at a lower portion of the acidic gas removing apparatus 98. The waste water contains impurities such as  $\text{SiO}_2$ ,  $\text{HF}$ , and others. The waste water is conducted to a neutralizer (not shown in the drawing) through the piping 37 by operating the waste water pump 60, and processed. In accordance with the present embodiment, the solid particles such as  $\text{SiO}_2$  are not brought into the catalyst layer 11 in the reactor 3, because the silicon components contained in the exhaust gas are previously removed by the silicon remover 2 as  $\text{SiO}_2$ . If the silicon remover 2 is not arranged,  $\text{SiO}_2$  is generated by the reaction expressed by the equation (1) with the water supplied from the water supplying piping 32 at a portion in a downstream from the joining point of the piping 31 and the water supplying piping 32. When the  $\text{SiO}_2$  is flowed into the catalyst layer 11, the following problems (1) and (2)

are caused:

(1) Pores formed on the catalysts are closed by the  $\text{SiO}_2$ .

(2) Intervals formed among the catalysts are choked. On account of the above problems (1) and (2), the surface of the catalyst is decreased, and the decomposition reaction of the PFC is decreased.

**[0048]** Furthermore, because of the above problem (2), the flow of the exhaust gas among the catalyst is decreased, and the contact of the catalyst with the exhaust gas is hindered. This causes also the decrease of the decomposition reaction of the PFC. In accordance with the present embodiment,  $\text{SiO}_2$  is previously removed from the exhaust gas by generating the reaction expressed by the equation (1) at the silicon remover 2, and accordingly, the above problems are not generated and decomposition efficiency on the PFC can be improved.

**[0049]** In accordance with the present embodiment, the decomposition processing of the PFC can be achieved with a high efficiency by using the catalyst, and the release of the PFC, which is one of the gases causing warming-up of the earth, into the atmosphere can be avoided. Furthermore, unreacted  $\text{CO}$  generated by the decomposition of  $\text{CF}_4$  with the catalyst can be converted to harmless  $\text{CO}_2$  by mixing air into the exhaust gas.

**[0050]** In accordance with the present embodiment,  $\text{CF}_4$  can be decomposed at a sufficiently lower temperature than the conventional combustion method. Accordingly, necessary utilities such as heat energy, water, and the like can be decreased. Application of the present embodiment to a semiconductor manufacturing plant is advantageous even in a safety aspect against fire hazard, because the temperature of the decomposed gas is low. The catalyst has a long life, and a recycle use of the catalyst is possible. Therefore, the operation cost of the plant can be decreased significantly in comparison with the reagent method.

**[0051]** When an end of life of the catalyst is reached, the catalyst cartridge 10 is replaced with a new catalyst cartridge. The exchanging operation is explained hereinafter referring to FIG. 7. The catalyst cartridge 10 is held by a flange 13 by fitting a protrusion 64 of a flange 63 to a groove 65 formed inside the flange 13. For detaching and attaching the catalyst cartridge 10, a cartridge detaching and attaching apparatus 66 is used. The cartridge detaching and attaching apparatus 66 comprises a lifter 68, a rotatable base 67 fixed rotatably to the lifter 68, and a rotary handle 69.

**[0052]** After detaching the cylinder 17, the baffle holder 21, and the cooling apparatus 22 from the casing 6, the cartridge detaching and attaching apparatus 66 is placed under the catalyst cartridge 10. The rotatable base 67 is elevated by the lifter 68. Rubber plate adhered on the surface of the rotatable base is contacted with the flange 63. The rotatable base is rotated by operation of the rotary handle 69. The rotating force is transmitted to the catalyst cartridge 10 via the rubber plate. When the protrusion 64 is moved to a designated position, the rotatable base 67 is stopped its moving, and the lifter is descended. The protrusion 64 is detached from the groove 65, and the catalyst cartridge 10 is disassembled from the flange 13 and withdrawn from the internal tube 7.

**[0053]** Then, a new catalyst cartridge 10 is placed on the rotatable base 67. The new catalyst cartridge 10 is inserted into the internal tube 7 by a reversal procedure of the detaching, and attached to the flange 13. The protrusion 64 of the new catalyst cartridge 10 is adjusted to the above designated position by rotating the rotatable base 67. After elevating the lifter 68 somewhat, the protrusion 64 is fitted to the groove 65 by rotating the rotatable base 67 reversely by operating the rotary handle 69. The cylinder 17, the baffle holder 21, and the cooling apparatus 22 are attached to the casing 6. Then, the PFC decomposition processing by the PFC decomposition processing unit 76 becomes usable again.

**[0054]** The exchange of the catalyst cartridge 10 can be performed readily by using the cartridge detaching and attaching apparatus 66. Because operators do not touch hot spent catalyst cartridge 10, the operators are protected from burning. Because the hot spent catalyst cartridge 10 can be detached readily, the time necessary for the exchanging operation of the catalyst cartridge 10 can be decreased significantly. Because spreading the catalyst particles and generating dusts by the exchanging operation can be prevented, the exchanging operation in the clean room becomes possible.

**[0055]** The present embodiment can be applied to the cases decomposing various substances indicated in Table 1 such as  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_4\text{F}_8$ . These substances can be decomposed at a reaction temperature of approximately  $700^\circ\text{C}$  using the alumina group catalyst. The present embodiment can be applied to the decomposition of  $\text{C}_2\text{F}_6$  contained in the exhaust gas from CVD apparatus, and PFC contained in the exhaust gas from etching apparatus for liquid crystal, in addition to the PFC contained in the exhaust gas from the dry etching apparatus in the semiconductor manufacturing plant.

**[0056]** An exhaust gas control system for dry etching apparatus in the semiconductor manufacturing, wherein a PFC processing apparatus of another embodiment of the present invention is applied, is explained hereinafter. The exhaust gas control system of the present embodiment is composed as same as the system indicated in FIG. 1 and FIG. 2 except each of the PFC processing apparatus such as 1, 1A, and the like are replaced with a PFC processing apparatus 1C indicated in FIG. 8. The PFC processing apparatus 1C has as same composition as the PFC processing apparatus 1, except the silicon remover 2 in the PFC processing apparatus 1 is replaced with a silicon removing apparatus 71,



and a return piping 75 is newly added. The silicon removing apparatus 71 comprises silicon removers 2 and 22. The silicon remover 72 comprises a spray 73, and a diffusion portion 74 filled with packing materials inside its vessel. The silicon remover 72 has a same composition as the silicon remover 2 indicated in FIG. 4. An outlet of the piping 29 is oriented downwards in the silicon remover 72. The ball check valve 27 is not provided at the outlet side of the silicon remover 72. The return piping 75 is connected to the piping 37 in the downstream of the waste water pump 60. The vessel of the silicon remover 72 is composed of corrosion resistant vinyl chloride, in order to prevent corrosion by HF.

**[0057]** The exhaust gas containing  $\text{CF}_4$ ,  $\text{SiF}_4$ , and the like is conducted into the vessel of the silicon remover 72 through the piping 29. The exhaust gas ascends in the vessel, and flows inside the vessel by diffusion through the diffusion portion 74. A part of waste water pumped out by the waste water pump 60 is sprayed through the spray 73 through the return piping 75. Concentration of respective F ions and Si ions in the waste water pumped out from the waste water pump 60 are less than tens ppm. The waste water has a sufficient performance for removing the Si and HF. In accordance with contacting a part of  $\text{SiF}_4$  contained in the exhaust gas with the sprayed waste water, the reaction expressed by the equation (1) occurs. The generated  $\text{SiO}_2$  is removed from the exhaust gas by the waste water. The HF is dissolved into the waste water.

**[0058]** The exhaust gas exhausted from the silicon remover 72 is conducted to the silicon remover 2. Fresh water supplied through the water supply piping 38 is sprayed through the spray 26 of the silicon remover 2. In accordance with contacting the residual  $\text{SiF}_4$  contained in the exhaust gas with the sprayed water, the reaction expressed by the equation (1) occurs in the silicon remover 2. The waste water containing the  $\text{SiO}_2$  and HF is conducted to the silicon remover 72 and mixed with the sprayed waste water from the spray 73. The mixed waste water is conducted to the bottom portion of the acidic gas removing apparatus 98 through the piping 35. The processes at other portions of the PFC processing apparatus 1C is as same as the processing in the PFC processing apparatus 1.

**[0059]** The PFC processing apparatus 1C generates the same advantages as the advantages obtained by the PFC processing apparatus 1. Furthermore, the PFC processing apparatus 1C has additional advantages as follows. That is, because the amount of the fresh water supplied through the water supply piping 38 in the PFC processing apparatus 1C is decreased, the amount of waste water conducted to the neutralizer (not shown in the figure) is decreased. Furthermore, since the reaction expressed by the equation (1) is generated at two portions in the silicon removers 2 and 72, the removing efficiency of the Si components such as  $\text{SiF}_4$  and the like contained in the exhaust gas is improved.

**[0060]** Another embodiment of the PFC decomposition processing unit is indicated in FIG. 9. The PFC decomposition processing unit 76A of the present embodiment comprises a heating apparatus 3A and a reactor 9A. The cylinder 17, the baffle holder 21, and the cooling apparatus 22 of the PFC decomposition processing unit 76 are also used in the PFC decomposition processing unit 76A by being arranged on the flange 13 in the casing 6 in the above order. The reactor 9A comprises a bottom portion 83 in an internal tube 79. A bottom plate 82 is provided at the bottom portion 83 as slidable. The catalyst layer 11 filled with the alumina group catalyst is formed on the bottom plate 82 and the bottom portion 83 in the internal tube 79. The alumina group catalyst is a catalyst containing  $\text{Al}_2\text{O}_3$  80 % and  $\text{NiO}_2$  20 % . A flange 81 of the internal tube 79 is fixed to the flange 13.

**[0061]** The heating apparatus 3A comprises an internal tube 77, the electric heater 4, and the insulating material 5 covering the electric heater 4. The electric heater 4 and the insulating material 5 are arranged between the internal tube 77 and the casing 6. A flange 78 of the internal tube 77 is fixed to the flange 80. A gap 16 is formed between the casing 6 and the flanges 78 and 81.

**[0062]** The catalyst which reaches at the end of life can be taken out from inside the internal tube 79 by detaching the cylinder 17, the baffle holder 21, and the cooling apparatus 22, and removing the bottom plate 82. Functions of the heating apparatus 3A and the reactor 9A are as same as the functions of the heating apparatus 3 and the reactor 9 of the PFC decomposition processing unit 76. The same advantages as the PFC decomposition processing unit 76 can be obtained by the PFC decomposition processing unit 76A.

**[0063]** An exhaust gas control system of the dry etching apparatus in the semiconductor manufacturing plant, whereto the other embodiment of the PFC processing apparatus of the present invention is applied, is explained hereinafter referring to FIG. 10, FIG. 11, and FIG. 12. In accordance with the exhaust gas control system of the present embodiment, plural PFC processing apparatus 1D are arranged in a clean room 54. This part differs from the embodiments indicated in FIG. 1 and FIG. 2. Each of the PFC processing apparatus 1D is connected to the separated piping 29, respectively.

**[0064]** A detailed composition of the PFC processing apparatus 1D is indicated in FIG. 11. The PFC processing apparatus 1D is a horizontal type, and comprises the silicon remover 2 and the PFC decomposition processing unit 76B. The silicon remover 2 is connected to the piping 29. The PFC decomposition processing unit 76B comprises the heating apparatus 3, a reactor 9B, and the cooling apparatus 22. The PFC decomposition processing unit 76B does not comprise the acidic gas removing apparatus 98. In accordance with the present embodiment, the acidic gas removing apparatus 98 is provided to the duct 45. The heating apparatus 3 of the PFC decomposition processing unit 76B is composed only by placing the heating apparatus 3 of the PFC decomposition processing unit 76 in a horizontal direction. The reactor 9B comprises plural holding plates 84 and 85, which are perforated with a large number of small holes, in the internal tube 7. The catalyst layer 11 is composed by packing and holding the alumina group catalyst

(containing  $\text{Al}_2\text{O}_3$  80 % and  $\text{NiO}_2$  20 %) between the holding plate 84 and the holding plate 85. A baffle plate 86 is arranged above the catalyst layer 11 as indicated in FIG. 12, and attached to inside the internal tube 7. The baffle 20 is provided inside the cooling apparatus 22. The functions of the heating apparatus 3, the reactor 9B, and the cooling apparatus 22 of the present embodiment are as same as the functions of the heating apparatus 3, the reactor 9, and the cooling apparatus 22 of the PFC decomposition processing unit 76.

[0065] The PFC processing apparatus 1D has the same advantages as the PFC processing apparatus 1, except no contribution of the acidic gas removing apparatus 98. Furthermore, the PFC processing apparatus 1D can be made compact, because it is arranged in a horizontal direction without providing the acidic gas removing apparatus 98. Accordingly, the PFC processing apparatus 1D can be installed in a ready-made semiconductor manufacturing plant, which scarcely have an extra margin in space for installing apparatus. That is, the PFC processing apparatus 1D can be installed in a piping area above the clean room 54. The PFC processing apparatus 1D requires only a small space for installation.

[0066] The catalyst in the catalyst layer 11 is descended somewhat in accordance with elapsing the time. therefore, a slight interval is formed between the upper surface of the catalyst layer 11 and the inner surface of the internal tube 7. Because the baffle plate 86 is arranged in the catalyst layer 11, by-passing undecomposed PFC gas through the slight interval to the cooling apparatus 22 can be prevented. The PFC gas is certainly passed through the catalyst layer 11 and decomposed.

[0067] Another embodiment of the exhaust gas control system of the dry etching apparatus in the semiconductor manufacturing plant is explained hereinafter. The exhaust gas control system of the present embodiment is composed by replacing each of the PFC processing apparatus in the exhaust gas control system indicated in FIG. 1 and FIG. 2 with the PFC processing apparatus 1E indicated in FIG. 13. The PFC processing apparatus 1E comprises the silicon remover 2, a PFC decomposition processing unit 76C, and an acidic gas removing apparatus 98, which is not shown in the figure 13. The PFC processing apparatus 1E is composed by replacing the PFC decomposition processing unit 78 in the PFC processing apparatus 1 with the PFC decomposition processing unit 76C.

[0068] A detailed composition of the PFC decomposition processing unit 76C is explained hereinafter. The PFC decomposition processing unit 76C differs from the PFC decomposition processing unit 76 in composition of the casing and the internal tube. The PFC decomposition processing unit 76C comprises a casing 88, a heating apparatus 3B for heating an internal tube 77, and a reactor 9B comprising a casing 89 and an internal tube 90. The heating apparatus 9B comprises the electric heater 4 and the insulating material 5 arranged between the casing 88 and the internal tube 77. In accordance with the reactor 9B, the catalyst cartridge 10 containing the catalyst layer 11 is inserted into the internal tube 90. The catalyst cartridge 10 is fitted to the flange at the lower end of the casing 89 as same as the PFC decomposition processing unit 76. The catalyst layer 11 is filled with the alumina group catalyst explained previously. The baffle holder 91 comprising the baffle 20 connects the reactor 9B and the cooling apparatus 22. The flanges of the casing 88, the internal tube 77, and the casing 89 are connected by bolts.

[0069] The PFC processing apparatus 1E generates the same advantages as the PFC processing apparatus 1. In accordance with detaching the connection of the above flanges, the heating apparatus 3B can be separated readily from the reactor 9B. Disassembling the catalyst cartridge 10 can be performed as same as the PFC decomposition processing unit 76.

[0070] Another embodiment of the exhaust gas control system of the dry etching apparatus in the semiconductor manufacturing plant is explained hereinafter. The exhaust gas control system of the present embodiment is composed by replacing each of the PFC processing apparatus in the exhaust gas control system indicated in FIG. 1 and FIG. 2 with the PFC processing apparatus 1F indicated in FIG. 14. The PFC processing apparatus 1F is composed by replacing the PFC decomposition processing unit 76 in the PFC processing apparatus 1C with the PFC decomposition processing unit 76C. In accordance with the PFC decomposition processing unit 76C, a heat exchanger 93 is arranged between the reactor 9 and the cylinder 17 of the PFC decomposition processing unit 76. A heat conducting tube 92 is arranged in the heat exchanger 93. The piping 32 is connected to the entrance side of the heat conducting tube 92. The piping 32A connected to the outlet side of the heat conducting tube 92 is connected to the piping 31 at a point in the upstream from the merging point of the piping 31 and the air supplying pipe 41.

[0071] In accordance with the present embodiment, the reaction water supplied from the piping 32 is heated by the exhaust gas at approximately 700 °C exhausted from the catalyst layer 11 to be steam during flowing through the heat conducting tube 92. The steam is introduced into the piping 31 through the piping 32A. The exhaust gas containing steam, air, and  $\text{CF}_4$ , which is one of the PFC, is conducted to the catalyst layer 11 via the heating apparatus 3. Then, the reaction expressed by the equation (2) is generated in the catalyst layer 11.

[0072] The PFC processing apparatus 1F generates the same advantages as the PFC processing apparatus 1C. Furthermore, in accordance with the present embodiment, the heat of the exhaust gas at approximately 700 °C exhausted from the catalyst layer 11 can be recovered by the heat exchanger 93. Accordingly, the heating capacity of the heating apparatus 3, and the amount of the cooling water to be supplied to the sprays 25 and 26 in the cooling apparatus 23 can be decreased. In accordance with the present embodiment, the amount of waste water to be con-

ducted to the neutralizer can be decreased smaller than that of the PFC processing apparatus 1C.

## Claims

1. A method for processing a perfluoride compound comprising the steps of:  
 removing silicon components from an exhaust gas containing the perfluoride compound and the silicon components,  
 adding at least any of water and steam to said exhaust gas containing the perfluoride compound,  
 heating the exhaust gas containing the perfluoride compound, and at least any of water and steam,  
 supplying the heated exhaust gas to a catalyst layer filled with a catalyst to decompose the fluoride compound contained in the exhaust gas by contacting with the catalyst,  
 cooling the exhaust gas containing decomposed gas generated by the decomposition of the perfluoride compound, and  
 releasing the cooled exhaust gas.
2. A method for processing a perfluoride compound as claimed in claim 1, wherein  
 said exhaust gas to be supplied to said catalyst layer is controlled to be heated at a designated temperature.
3. A method for processing a perfluoride compound as claimed in claim 2, wherein  
 said designated temperature is in the range of 650 °C ~ 750 °C.
4. A method for processing a perfluoride compound as claimed in claim 1, wherein  
 an acidic gas is removed from said cooled exhaust gas.
5. A method for processing a perfluoride compound as claimed in claim 1, wherein  
 said silicon components is removed from said exhaust gas by contacting the exhaust gas containing said silicon components with water.
6. A method for processing a perfluoride compound as claimed in claim 5, wherein  
 said exhaust gas containing the decomposed gas is cooled by heat exchanging said exhaust gas with cooling water.
7. A method for processing a perfluoride compound as claimed in claim 6, wherein  
 said removal of the silicon components is performed by using a first silicon component removing apparatus and a second silicon component removing apparatus,  
 said exhaust gas exhausted from said first silicon component removing apparatus is supplied to said second silicon component removing apparatus,  
 said exhaust gas is contacted with water in the second silicon component removing apparatus, and  
 said exhaust gas containing the silicon components is contacted with both waste water from said second silicon component removing apparatus and said cooling water contacted with said exhaust gas containing said decomposed gas in said first silicon component removing apparatus.
8. A method for processing a perfluoride compound as claimed in claim 1, wherein  
 said steam is generated by heat exchange of water with said exhaust gas exhausted from said catalyst layer.
9. A method for processing a perfluoride compound as claimed in claim 1, wherein  
 said catalyst is an alumina group catalyst.

10. A method for processing a perfluoride compound as claimed in claim 1, wherein

said exhaust gas is an exhaust gas exhausted from semiconductor manufacturing apparatus.

5 11. A perfluoride compound processing apparatus comprising:

a silicon component removing apparatus for removing a silicon component from an exhaust gas containing a perfluoride compound and said silicon component,  
a heating apparatus for heating said exhaust gas containing said perfluoride compound, whereinto any of water and steam is added after exhausted from said silicon component removing apparatus,  
10 a catalyst layer filled with a catalyst for decomposing said perfluoride compound contained in said exhaust gas exhausted from said heating apparatus, and  
a cooling apparatus for cooling said exhaust gas exhausted from said catalyst layer.

15 12. A perfluoride compound processing apparatus as claimed in claim 11, further comprises

a temperature detector for detecting a temperature of said exhaust gas exhausted from said catalyst layer, and  
a controller for controlling said heating apparatus based on the temperature detected by the temperature detector.

20 13. A perfluoride compound processing apparatus as claimed in claim 11, further comprises

an acidic gas removing apparatus for removing the acidic gas contained in said exhaust gas exhausted from said cooling apparatus.

25 14. A perfluoride compound processing apparatus as claimed in claim 11, wherein

said silicon component removing apparatus comprises a spray apparatus for spraying water.

30 15. A perfluoride compound processing apparatus as claimed in claim 14, wherein

said cooling apparatus comprises a spray apparatus for spraying cooling water for cooling said exhaust gas.

35 16. A perfluoride compound processing apparatus as claimed in claim 15, wherein

said silicon component removing apparatus comprises a first silicon component removing apparatus, and a second silicon component removing apparatus, whereinto said exhaust gas from said first silicon component removing apparatus is supplied,  
a first spray apparatus for spraying water is provided inside said second spray apparatus, and  
40 a second spray apparatus for spraying both water sprayed from said first spray apparatus and water sprayed from said spray apparatus of said cooling apparatus.

17. A perfluoride compound processing apparatus as claimed in claim 11, wherein

45 a check valve for preventing said exhaust gas from flowing back into said silicon component removing apparatus from said heating apparatus is provided in a path conducting said exhaust gas from said silicon component removing apparatus to said heating apparatus.

50 18. A perfluoride compound processing apparatus as claimed in claim 11, wherein

said heater, said catalyst layer, and said cooling apparatus are formed in an integral body structure in the above order.

55 19. A perfluoride compound processing apparatus as claimed in claim 18, wherein

said integral body structure is formed by arranging said heater, said catalyst layer, and said cooling apparatus in a horizontal direction, and a baffle member for disturbing a flow of undecomposed perfluoride compound is provided at a portion above said catalyst layer.

20. A perfluoride compound processing apparatus as claimed in claim 11, wherein

a heat exchanger for exchanging heat between the exhaust gas exhausted from said catalyst layer and water, and generating said steam is provided between said catalyst layer and said cooling apparatus.

21. A perfluoride compound processing apparatus as claimed in claim 11, further comprising

a cartridge, wherein said catalyst layer is formed inside, and  
a casing wherein said cartridge is attached detachably, wherein  
said heater, said casing, and said cooling apparatus are formed in an integral body structure in the above order.

22. A perfluoride compound processing apparatus as claimed in claim 21, further comprising

a reactor which comprises said cartridge, an internal tube wherein said cartridge is contained, and said casing, wherein  
said casing of said reactor is shared with a casing of said heater.

23. A perfluoride compound processing apparatus as claimed in claim 14, wherein

an exhaust gas inlet portion for supplying said exhaust gas containing a perfluoride compound and a silicon component to said silicon component removing apparatus is extended into said silicon component removing apparatus, and  
a gas outlet opening of said exhaust gas inlet portion is provided at a position lower than said spray apparatus, and said gas outlet opening is oriented downwards in said silicon component removing apparatus.

24. A perfluoride compound processing apparatus as claimed in claim 23, wherein

a diffusion portion for diffusing sprayed water from said spray apparatus is provided inside said silicon component removing apparatus between said spray apparatus and said exhaust gas inlet portion.

25. An exhaust gas processing apparatus of semiconductor manufacturing apparatus comprising:

a silicon component removing apparatus for removing a silicon component from an exhaust gas containing a perfluoride compound and said silicon component,  
a heating apparatus for heating said exhaust gas containing said perfluoride compound, where to any of water and steam is added after exhausted from said silicon component removing apparatus,  
a catalyst layer filled with a catalyst for decomposing said perfluoride compound contained in said exhaust gas exhausted from said heating apparatus, and  
a cooling apparatus for cooling said exhaust gas exhausted from said catalyst layer.

26. An exhaust gas processing apparatus of semiconductor manufacturing apparatus as claimed in claim 25, wherein

said heating apparatus, said catalyst layer, and said cooling apparatus are formed in an integral body structure in the above order, and  
said integral body structure of said heating apparatus, said catalyst layer, and said cooling apparatus is installed in a building, wherein said semiconductor manufacturing apparatus is installed.

FIG. 1

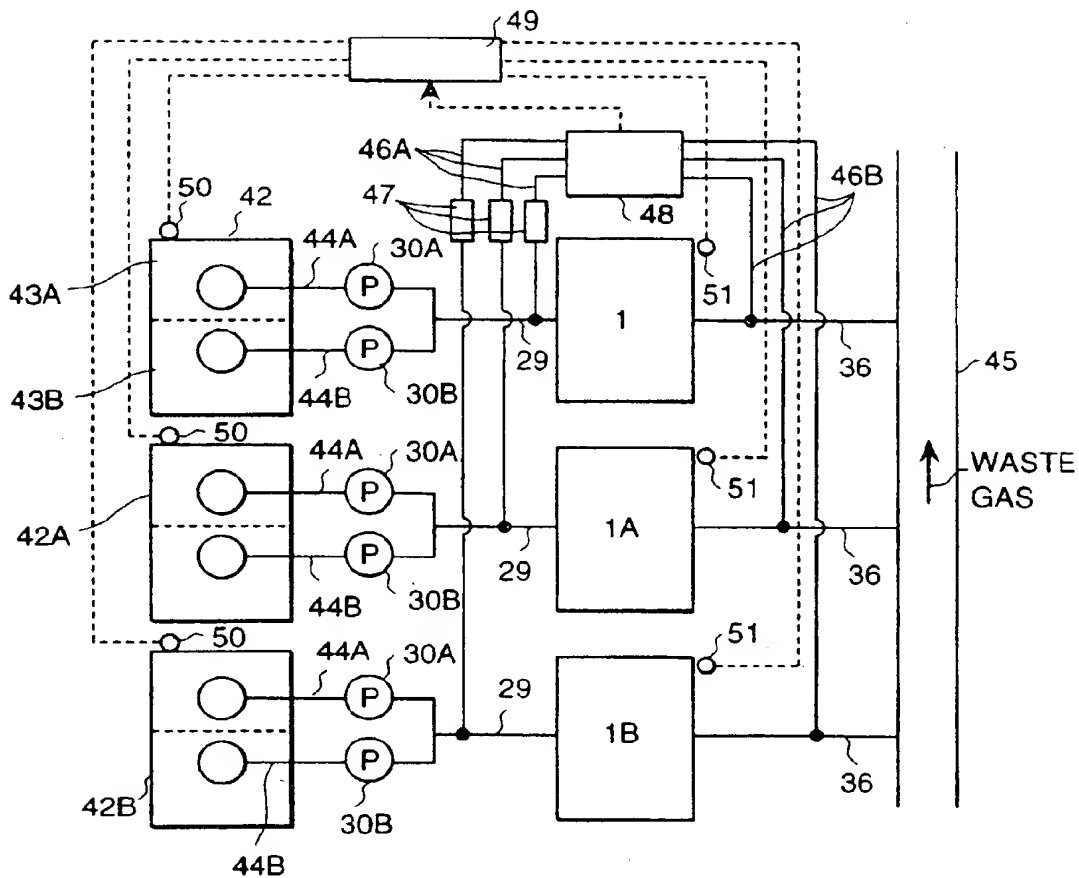


FIG. 2

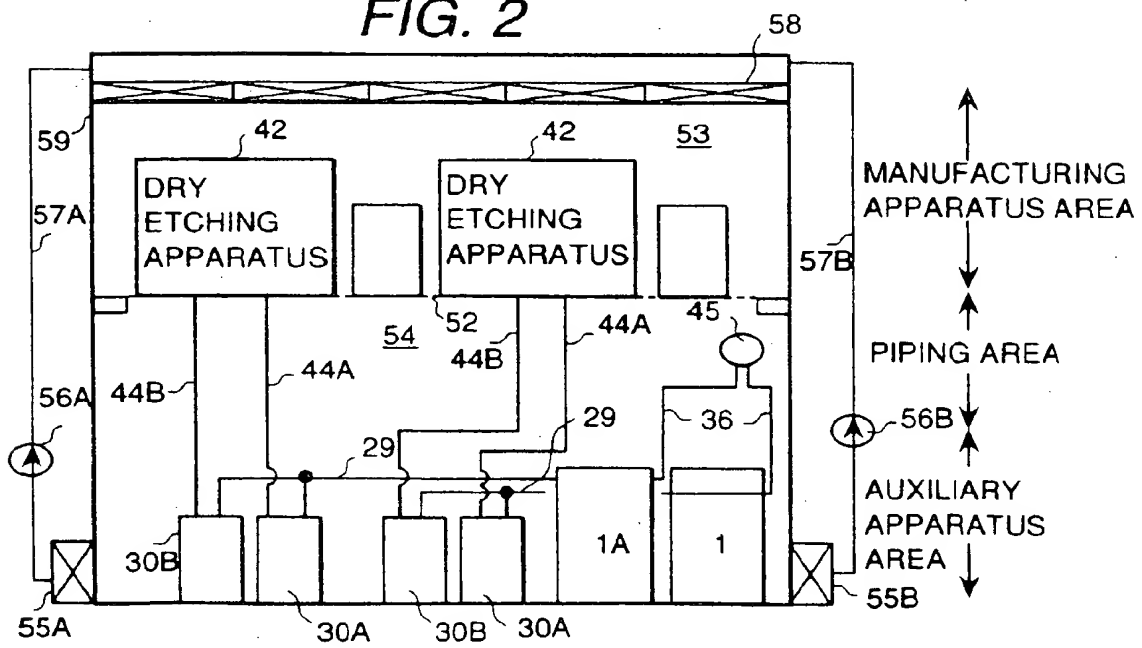


FIG. 3

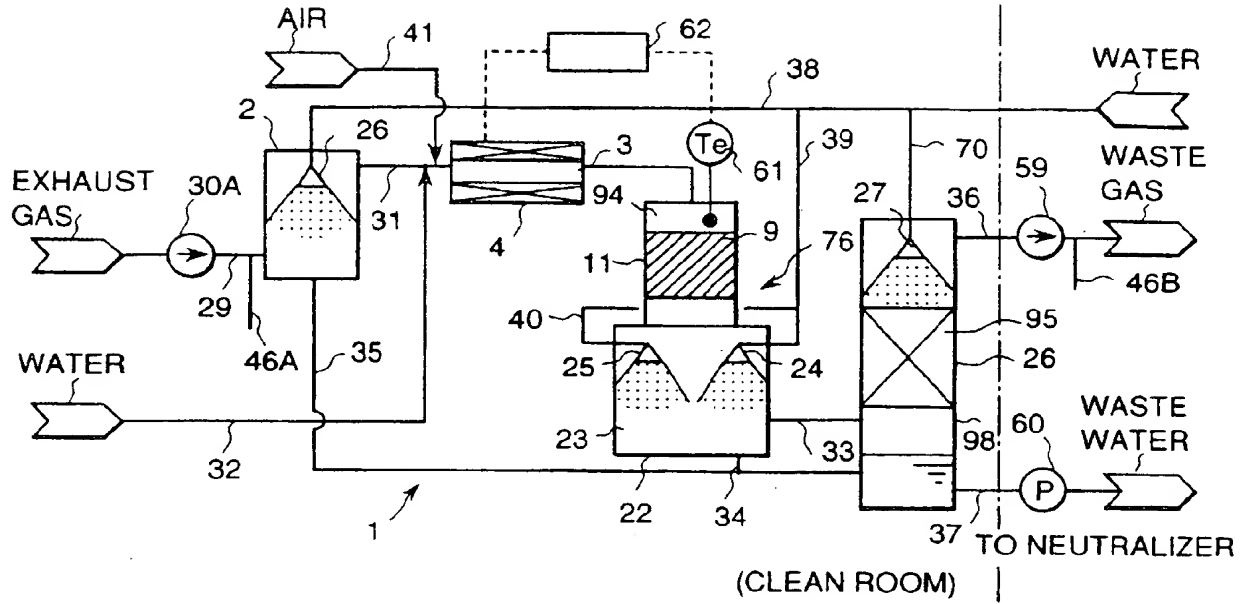


FIG. 4

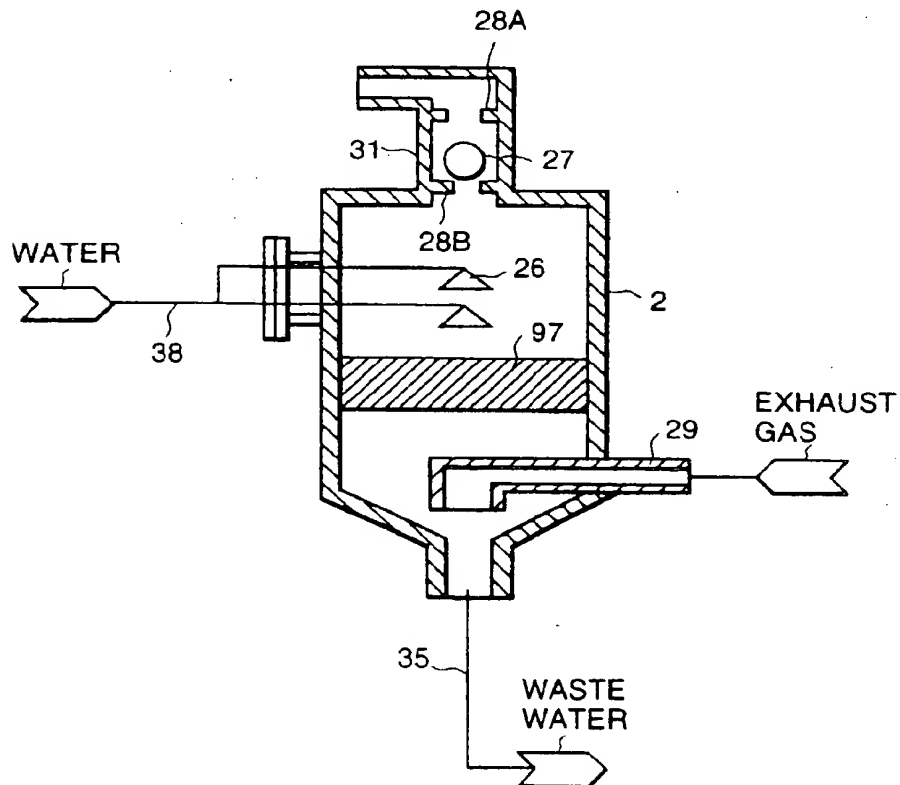


FIG. 5

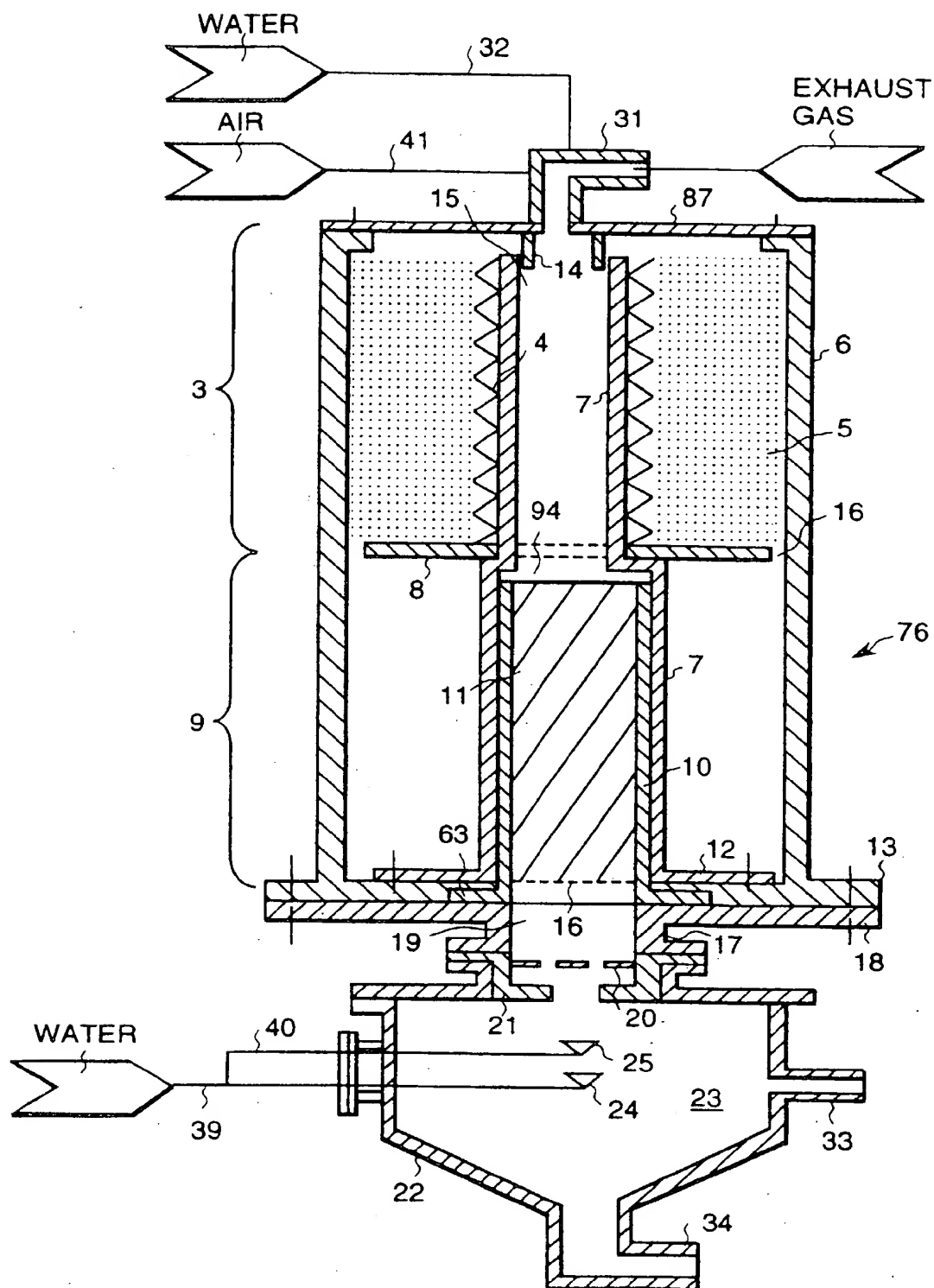




FIG. 6

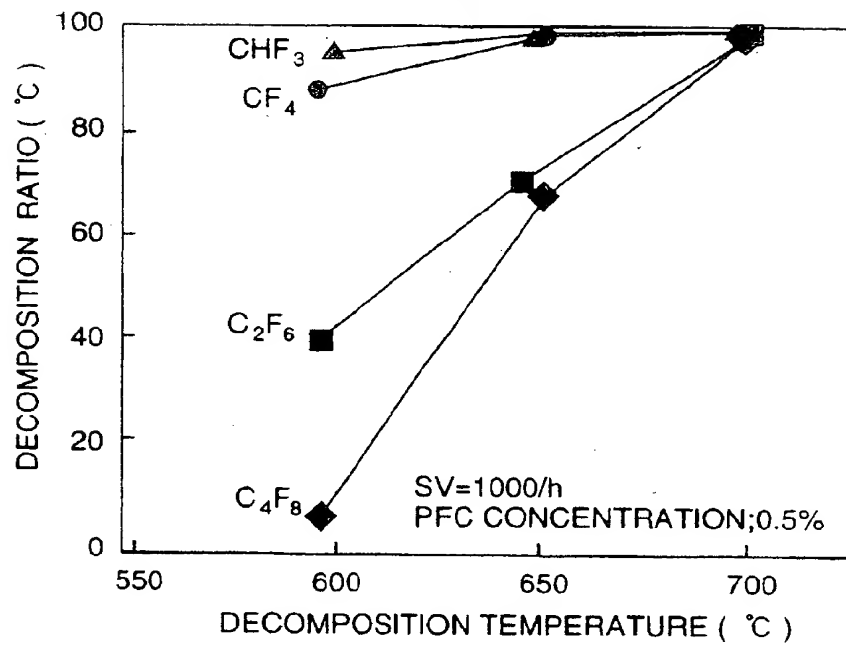


FIG. 7

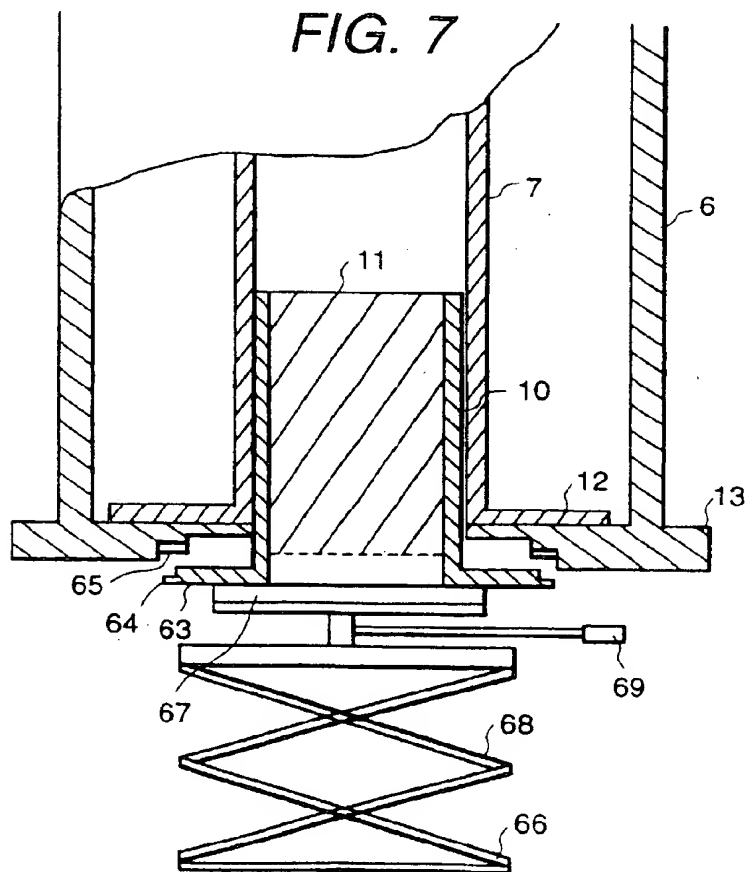


FIG. 8

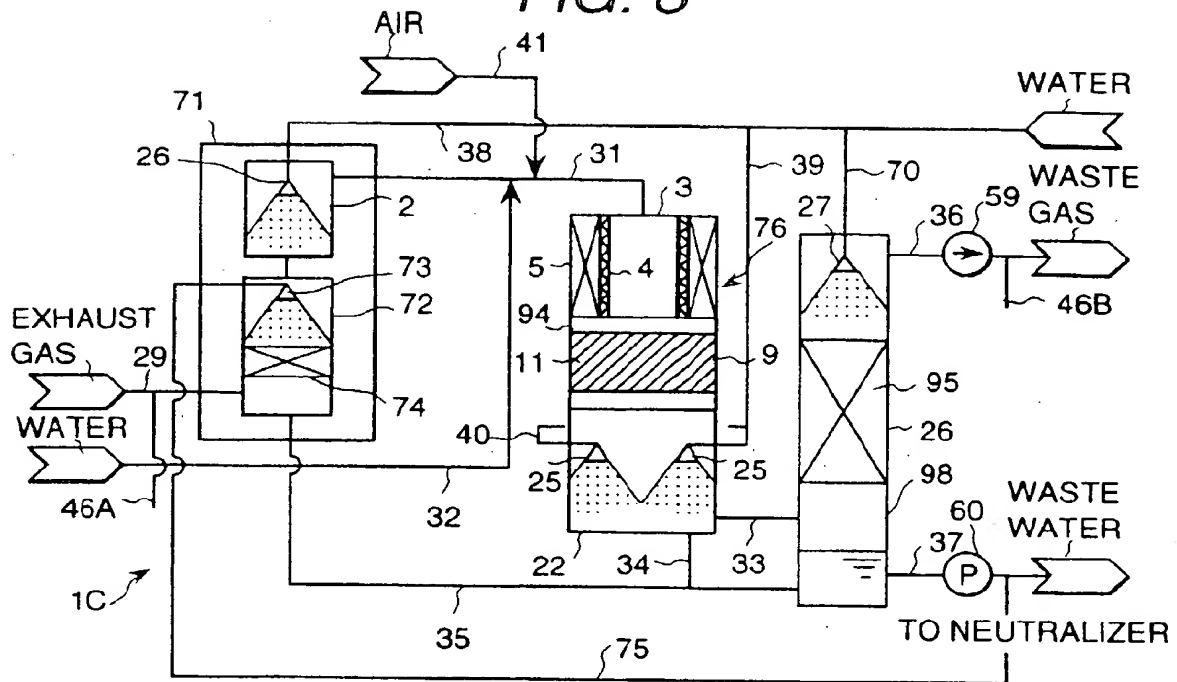


FIG. 9

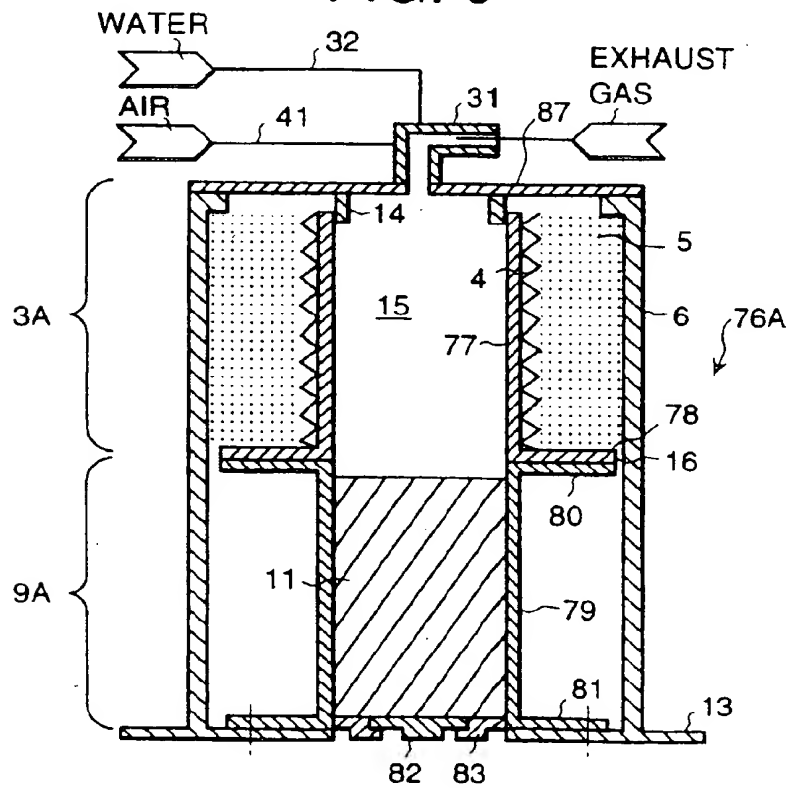


FIG. 10

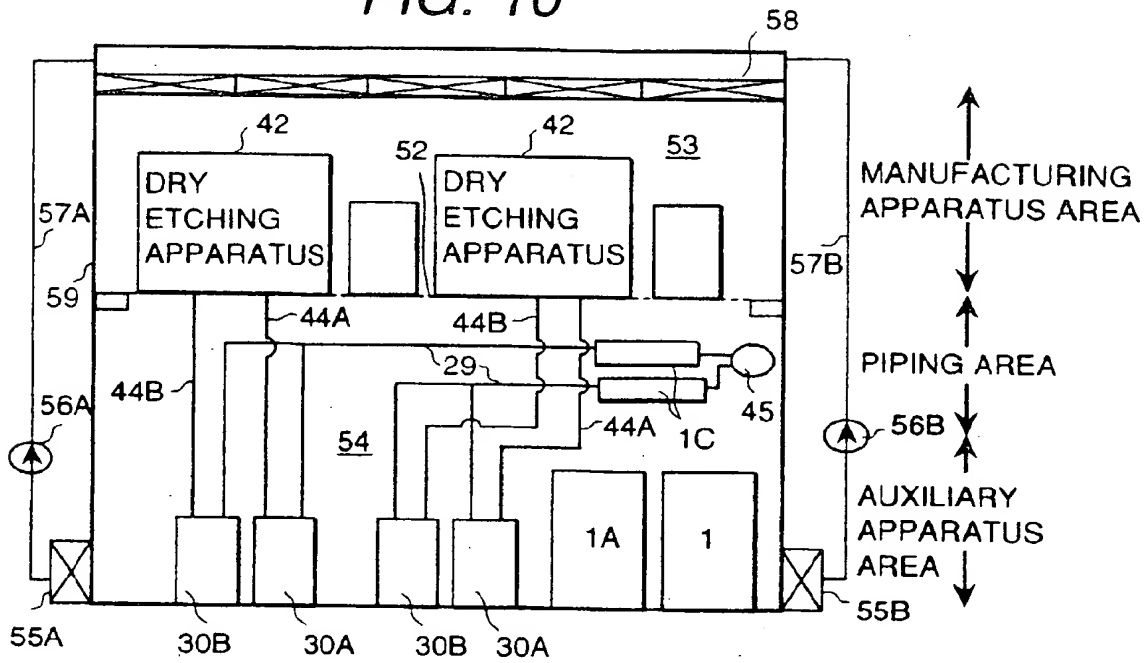


FIG. 11

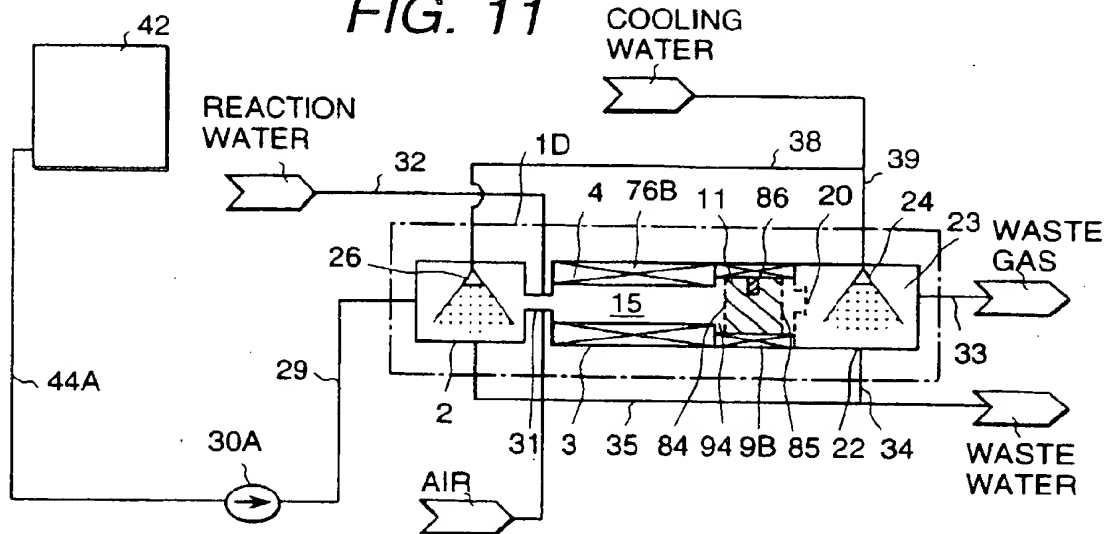


FIG. 12

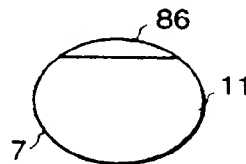


FIG. 13

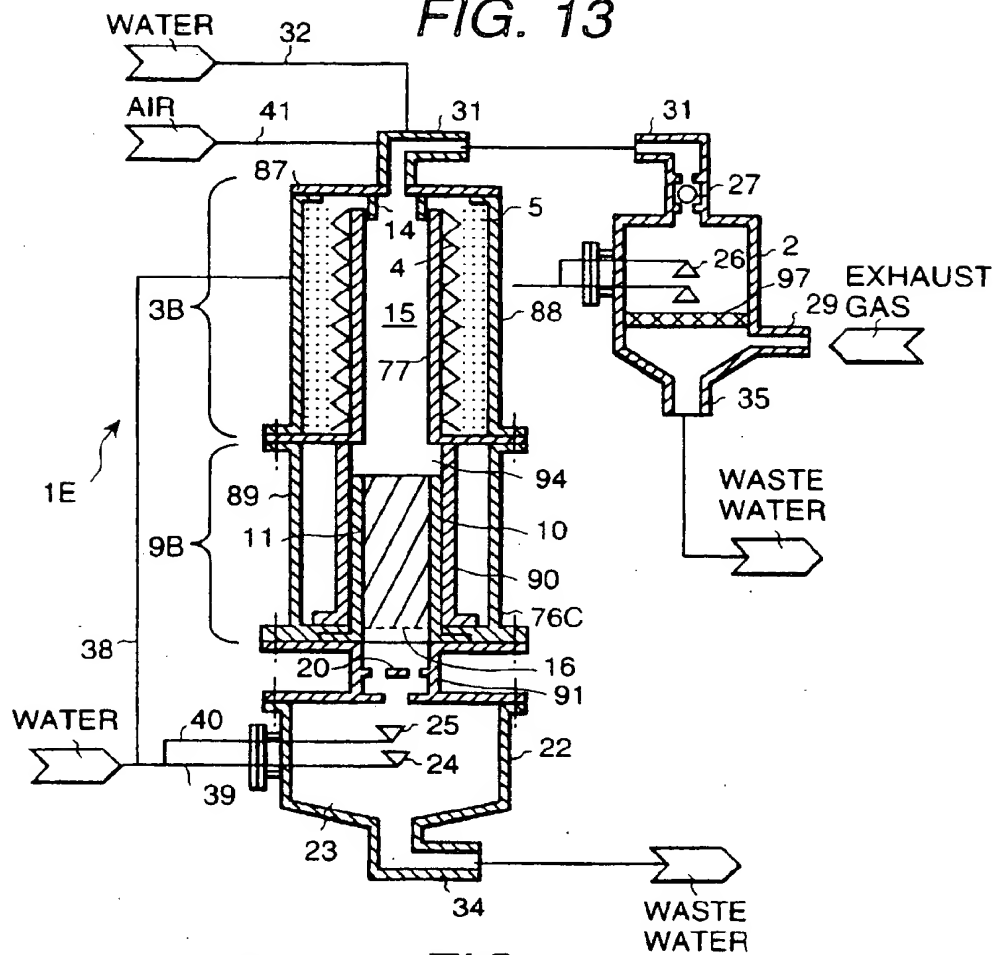
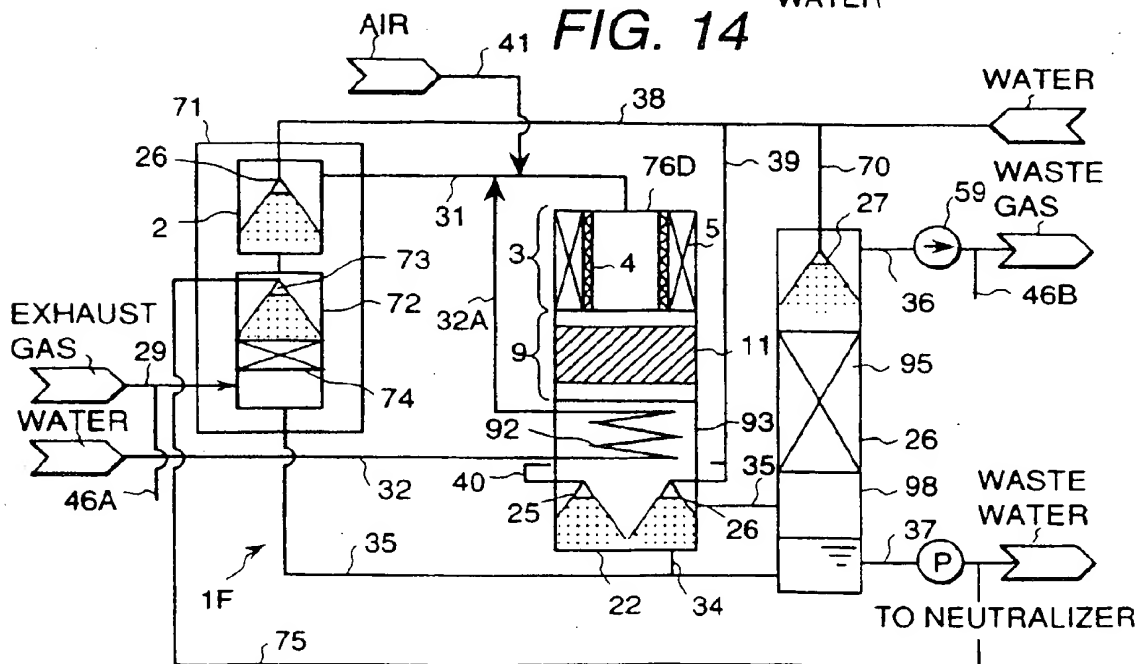
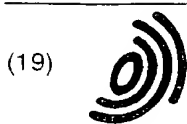


FIG. 14





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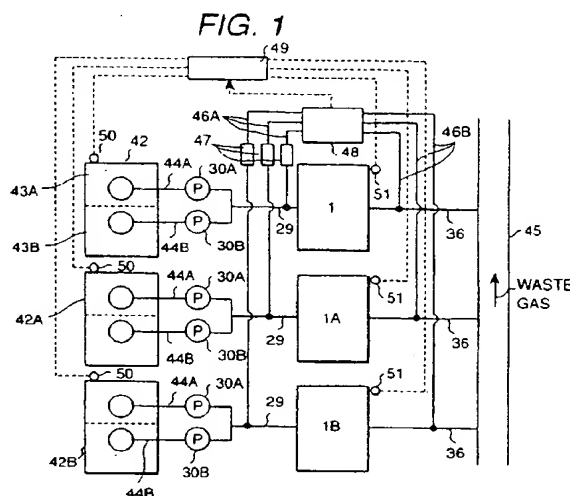
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Hitachioota-shi, Ibaraka 313-0038 (JP)  
• Tomiyama, Takayuki  
2-chome, Hitachi-shi, Ibaraki 316-0004 (JP)  
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Nishiibaraki-gun, Ibaraki 309-1738 (JP)  
• Tamata, Shin  
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(54) A method for processing perfluorocarbon and an apparatus therefor

(57) An exhaust gas containing a perfluoride compound (PFC) and  $\text{SiF}_4$  is conducted into a silicon remover and contacted with water. A reaction water supplied from a water supplying piping and air supplied from an air supplying piping are mixed with the exhaust gas exhausted from the silicon remover. The exhaust gas containing water, air, and  $\text{CF}_4$  is heated at  $700^\circ\text{C}$  by a heater. The exhaust gas containing PFC is conducted to a catalyst layer filled with an alumina group catalyst. The PFC is decomposed to HF and  $\text{CO}_2$  by the catalyst. The exhaust gas containing HF and  $\text{CO}_2$  at a high temperature exhausted from the catalyst layer is cooled in a cooling apparatus. Subsequently, the exhaust gas is conducted to an acidic gas removing apparatus to remove HF. In accordance with the present invention, the silicon component is removed from the exhaust gas before introducing the exhaust gas into the catalyst layer. Therefore, surface of the catalyst can be utilized effectively, and the decomposition reaction of the perfluoride compound can be improved.





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 9136

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
E	EP 0 885 648 A (HITACHI LTD) 23 December 1998 (1998-12-23)  * page 2, line 46 - line 50 * * page 3, line 55 - page 4, line 5; claim 1 *	1, 3, 4, 9-11, 13, 25, 26	B01D53/86 B01D53/14 H01L21/00
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 119 (C-579), 23 March 1989 (1989-03-23) & JP 63 291625 A (TOYO SANSO KK), 29 November 1988 (1988-11-29) * abstract *	1, 11, 25	
A	US 5 649 985 A (IMAMURA HIROSHI) 22 July 1997 (1997-07-22) * column 6, line 45 - line 51; claim 1 * * column 2, line 39 - line 43 *	1, 11, 25, 26	
A	EP 0 642 809 A (CHEMIE LINZ GMBH) 15 March 1995 (1995-03-15) * page 1, line 27 - line 32 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 October 1999	Examiner Faria, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (01/97) (P&C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 9136

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-10-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0885648	A	23-12-1998	JP	11070322 A	16-03-1999
JP 63291625	A	29-11-1988	NONE		
US 5649985	A	22-07-1997	US	5716428 A	10-02-1998
EP 0642809	A	15-03-1995	AT	404431 B	25-11-1998
			AT	181993 A	15-04-1998
			US	5710359 A	20-01-1998